

Carbonate Pyrolysis. Part IV.¹ The Stereochemistry of Elimination; a ¹³C Nuclear Magnetic Resonance Study

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A convenient ¹³C n.m.r. analysis of the mixed butenes from either *threo*- or *erythro*-methyl 2-deuterio-1-methylpropyl carbonates shows the elimination to be *cis*.

THE pyrolysis of dialkyl carbonates has been investigated kinetically by two groups of workers,^{1,2} and the aralkyl series has been studied by Smith *et al.*³ With the exception of the dimethyl derivative, all these carbonates undergo a simple β -elimination by a unimolecular mechanism, with good first-order kinetics. The activation parameters, without exception, point to a concerted cyclic process, the stereochemistry of which should be *cis*. The purpose of the present work was to examine the stereochemistry of dialkyl carbonate pyrolysis as further evidence for the mechanism of the reaction.

The stereochemistry of the closely related acetate pyrolysis has been examined in three ways. (i) The kinetic method is exemplified by *trans*-2-methylindan-1-yl acetate which decomposes rapidly and completely to 2-methylindene at 450°, while its *cis*-counterpart requires a temperature of 650° for decomposition.^{4,5} In the

indane system the neighbouring groups are completely eclipsed and there is no reason to doubt the method.

(ii) The direction of elimination in cyclic systems has been widely used, but is of doubtful merit. Thus models show that in *cis*-2-methylcyclohexyl acetate the 2-hydrogen atom which is *trans* to the acetate group subtends the same dihedral angle to it as do the two 6-hydrogen atoms. It is not surprising therefore that 25% of 1-methylcyclohexene is obtained in addition to 75% 3-methylcyclohexene.⁶

(iii) A conformational approach was introduced for xanthates by Cram⁷ and was developed by use of isotopic substitution by Curtin and Kellom.⁸ These authors' results were not entirely conclusive, but a later use of the same method based on DL-*threo*- and DL-*erythro*-3-deuteriobutan-2-ol was entirely successful.⁹ The butenes produced from pyrolysis of each isomeric

¹ Part III, D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 2359.

² A. S. Gordon and W. P. Norris, *J. Phys. Chem.*, 1965, **69**, 3013.

³ G. G. Smith, K. K. Lum, J. A. Kirby, and J. Posposil, *J. Org. Chem.*, 1969, **34**, 2090.

⁴ E. R. Alexander and A. Mudrak, *J. Amer. Chem. Soc.*, 1950, **72**, 1810.

⁵ E. R. Alexander and A. Mudrak, *J. Amer. Chem. Soc.*, 1950, **72**, 3194.

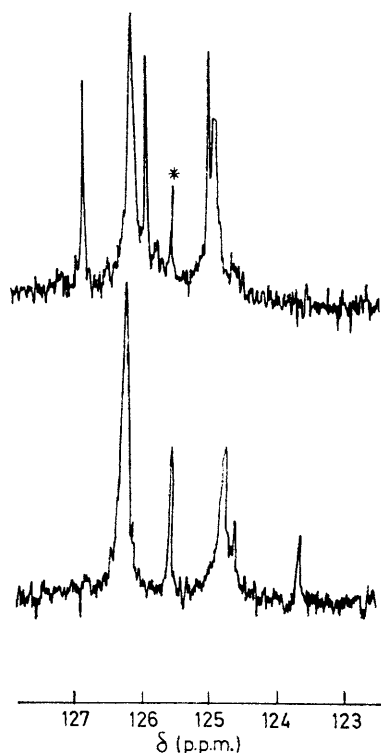
⁶ R. T. Arnold, G. G. Smith, and R. M. Dodson, *J. Org. Chem.*, 1950, **15**, 1256.

⁷ D. J. Cram, *J. Amer. Chem. Soc.*, 1949, **71**, 3883.

⁸ D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.*, 1953, **75**, 6011.

acetate were collected and separated by g.l.c.; the deuterium content of each pure isomer was then estimated by mass spectrometry.

We report here an extension of this approach which allows us to assess the position and extent of deuteriation in each of the three isomeric butenes obtained from the pyrolysis¹⁰ of the two diastereomeric methyl 2-deuterio-1-methylpropyl carbonates, without recourse to g.l.c. separation. Direct analysis of the proton noise-decoupled ¹³C n.m.r. spectra of the butene mixtures reveals clearly the position and extent of deuteriation. Thus in the case of both product mixtures, the signal at 26.9 p.p.m. due to the C-3 carbon in but-1-ene consists of a clean 1 : 1 : 1 triplet, as expected for a CHD fragment, the proton coupling being removed by noise-decoupling. The value of ¹J_{CD}, 19.5 Hz, is of the expected magnitude.¹¹ In the case of the but-2-enes, it can clearly be seen (Figure) that in the product mixture from the *erythro*-isomer, *cis*-but-2-ene is completely undeuteriated within the limits of detection, as demonstrated by the absence of C-D coupling effects on the carbon resonance at 125.0 p.p.m. The *trans*-but-2-ene

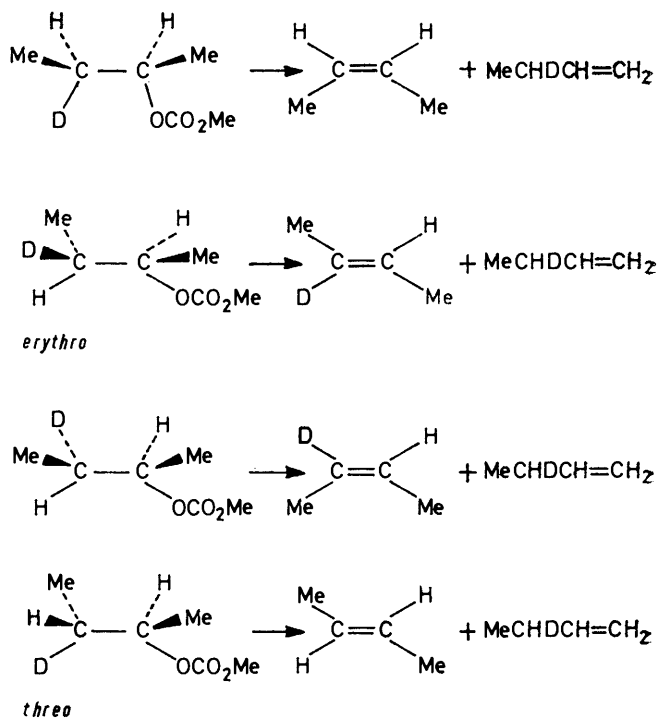


C-2 Resonances of *cis*- and *trans*-but-2-enes derived from *erythro*- (top) and *threo*-carbonates (bottom). The asterisked line, which overlaps with the highest frequency C-2 line of *cis*-[2-²H]but-2-ene (bottom) is due to an unidentified impurity present in the CD₃COCD₃ solvent

however, is clearly monodeuteriated on the C-2 carbon, as shown by the presence of a slightly broadened resonance for C-3 at 126.2 p.p.m., and a 1 : 1 : 1 triplet at

⁹ P. S. Skell and W. L. Hall, *J. Amer. Chem. Soc.*, 1964, **86**, 1557.

126.0 p.p.m. due to C-2. Both the value of ¹J_{CD} for C-2, 23.0 Hz, and for the isotope shift of C-3, ca. 0.2 p.p.m., are as expected. The reverse is true of the



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but-2-enes from pyrolysis of the *threo*-carbonate. In this case, *trans*-but-2-ene is deuterium free as shown by the singlet resonance at 126.3 p.p.m. for C-2, while *cis*-but-2-ene is monodeuteriated at C-2 with a broadened singlet at 124.8 p.p.m. due to C-3 and the isotopically shifted 1 : 1 : 1 triplet at 124.6 p.p.m. (¹J_{CD} 23.5 Hz) due to C-2. These results show conclusively that the stereochemistry of the elimination is, within the limits of detection, purely *cis* (Scheme). Close examination of the spectra reveals that in [2-²H]but-2-ene each isomer exhibits a small but real deuterium isotope shift to higher field for the C-3 carbon, in addition to the larger upfield shift experienced by the deuteriated (C-2) carbon. Similar geminal isotope effects have been observed¹¹ in other systems.

EXPERIMENTAL

erythro-3-Bromobutan-2-ol.—*trans*-But-2-ene (56 g) was passed during 2 h into a flask containing *N*-bromosuccinimide (160 g), water (800 ml), and 4*N*-H₂SO₄ (12 ml), and equipped with a stirrer and dry-ice condenser. The lower layer that formed was separated, dried, and distilled to afford the bromo-alcohol (100 g, 66%), b.p. 66–68° at 30 mmHg.

threo-3-Bromobutan-2-ol. This compound was prepared in the same way as the *erythro*-isomer using *cis*-but-2-ene in 65% yield, b.p. 66–68° at 30 mmHg.

¹⁰ D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 926.

¹¹ J. B. Stothers, in 'Topics in Carbon-13 NMR Spectroscopy,' ed. G. C. Levy, Wiley-Interscience, New York, 1974, ch. 6.

cis- and trans-2,3-Dimethyloxirans.—These were prepared in 60% yields from the *threo-* and *erythro-3-bromobutan-2-ols* respectively, by the method of Winstein and Lucas,¹² b.p. 60° (*cis*-isomer) and 54° (*trans*-isomer).

Diastereoisomeric [3-²H]Butan-2-ols.—Each oxiran was added to an excess of lithium aluminium deuteride in ether with stirring. The excess of hydride was destroyed by

the carbonates, Cr(acac)₃ (ca. 10 mg) was added to the solution¹³ to shorten the T₁ values for the deuteriated carbon atoms, and to suppress the nuclear Overhauser enhancement effect (NOE) from the proton noise-decoupling which was employed in the generation of all spectra recorded in this paper. The combination of short T₁ values and suppressed NOE allows integration of the spectra. The

TABLE I
¹³C N.m.r. data for diastereoisomeric carbonates and isomeric butenes

| Compound | Butyl carbon atoms | | | | Others | |
|--|--------------------|--|---|--------|--------|-------------------|
| | C-1 | C-2 | C-3 | C-4 | C=O | O-CH ₃ |
| [3- ² H]But-1-ene | 113.6 | 140.9 | 26.9 (¹ J _{CD} 19.5 Hz) | 13.4 | | |
| <i>cis</i> -But-2-ene | 12.7 * | 125.0 | 125.0 | 12.7 * | | |
| <i>cis</i> -[2- ² H]But-2-ene | 12.7 * | 124.6 (¹ J _{OD} 23.5 Hz) | 124.8 | 12.7 * | | |
| <i>trans</i> -But-2-ene | 18.2 * | 126.3 | 126.3 | 18.2 * | | |
| <i>trans</i> -[2- ² H]But-2-ene | 18.2 * | 126.0 (¹ J _{CD} 23.0 Hz) | 126.2 | 18.2 * | | |
| <i>erythro</i> -Carbonate | 19.4 | 76.5 | 28.4 (¹ J _{CD} 29.5 Hz) | 9.5 | 155.6 | 54.4 |
| <i>threo</i> -Carbonate | 19.4 | 76.5 | 28.4 (¹ J _{CD} 19.5 Hz) | 9.5 | 155.6 | 54.4 |

* At the resolution employed for these measurements (± 0.15 p.p.m.), no definite assessment of β -isotope shifts could be made.

dropwise addition of saturated aqueous magnesium sulphate solution, and the ether layer was separated, dried and distilled to afford the deuteriated alcohol (*threo*-isomer from the *cis*-oxiran, *erythro*-isomer from the *trans*-oxiran). Both were obtained in ca. 80% yield, and both had b.p. 99°.

Diastereoisomeric Methyl 2-Deuterio-1-methylpropyl Carbonates.—Each alcohol (3.5 g) and methyl chloroformate (5.6 g) in ether (20 ml) were stirred under nitrogen for 2 h while dry pyridine (4 ml) was added dropwise. The mixture was stirred overnight, washed with water, and with dilute HCl, and the ethereal layer separated and dried. Distillation gave the carbonates, (ca. 5 g, 70%) both with b.p. 138—139°. The ¹³C spectra of the carbonates were virtually identical (Table I).

Pyrolysis of Diastereoisomeric Carbonates.—The pyrolyses were carried out in the flow apparatus previously described.¹⁰ A 3 ft Chromasorb 102 preparative column with a 20:1 outlet splitter was used in the g.l.c. equipment. The butene mixtures were trapped using liquid nitrogen, and transferred to a vacuum line. They were then distilled, together with deuterioacetone, into 10 mm n.m.r. tubes containing Cr(acac)₃ (10 mg), and the tubes were sealed off. Solutions containing ca. 200 mg of butene mixture in 3 ml deuteriated acetone were prepared in this way.

¹³C N.m.r. Spectra.—Spectra were recorded using a JEOL PS-100 spectrometer operating in the Fourier transform mode, and employing an internal deuterium lock. In the case of the butene mixtures obtained from pyrolysis of

results derived from the n.m.r. measurements are shown in Table I. The relative yields of the olefinic products derived from integration of the n.m.r. spectra are given in Table 2

TABLE 2
Olefin yields^a from carbonate^b and acetate^c pyrolysis

| Compound | But-1-ene (%) | <i>trans</i> -But-2-ene (%) | <i>cis</i> -But-2-ene (%) |
|--|---------------|-----------------------------|---------------------------|
| Undeuteriated carbonate | 58 | 28 | 14 |
| <i>erythro</i> -[3- ² H]Carbonate | 61 (60) | 29 (30) | 10 (10) |
| <i>threo</i> -[3- ² H]Carbonate | 64 (60) | 20 (20) | 16 (20) |
| Undeuteriated acetate | 57 | 28 | 15 |
| <i>erythro</i> -[3- ² H]Acetate | 61 | 30 | 9 |
| <i>threo</i> -[3- ² H]Acetate | 63 | 19 | 18 |

^a G.l.c. analysis, with results from n.m.r. integration in parentheses. ^b This work. ^c Ref. 9.

together with those obtained by g.l.c. analysis, and it can be seen that the agreement is reasonable. The ratio of butenes obtained from methyl 1-methylpropyl carbonate differs slightly from that previously reported for bis-1-methylpropyl carbonate,¹⁴ and is indistinguishable from that given by the acetate. k_H/k_D is 1.4—1.5, compared with 1.6—1.7 for the acetate.⁹

[5/1727 Received, 8th September, 1975]

¹³ R. Freeman, K. G. R. Pachler, and G. N. LaMar, *J. Chem. Phys.*, 1971, **55**, 4586.

¹⁴ D. B. Bigley and C. M. Wren, *J.C.S. Perkin II*, 1972, 1744.

¹² S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, 1939, **61**, 1580.